

Detection of poly- and perfluoroalkyl substances (PFASs) in U.S. drinking water linked to industrial sites, military fire training areas and wastewater treatment plants

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25 **Notes:**

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Abstract

Contamination of drinking water with poly- and perfluoroalkyl substances (PFASs) poses risks to the developmental, immune, metabolic, and endocrine health of consumers. We present a spatial analysis of 2013-2015 national drinking water PFAS concentrations from the U.S. Environmental Protection Agency's (US EPA) third Unregulated Contaminant Monitoring Rule (UCMR3) program. Abundance of industrial sites that manufacture or use these compounds, military fire training areas, and wastewater treatment plants are all significant predictors of PFAS detection frequencies and concentrations in public water supplies. Among samples with detectable PFAS levels, each additional military site within a watershed's 8-digit hydrologic unit is associated with a 20% increase in PFHxS, a 10% increase in both PFHpA and PFOA, and a 35% increase in PFOS. Abundance of civilian airports with personnel trained in the use of aqueous film-forming foams (AFFFs) is significantly associated with the detection of PFASs above the minimum reporting level. We find drinking water supplies for 6 million U.S. residents exceed US EPA's lifetime health advisory (70 ng/L) for PFOS and PFOA. Lower analytical reporting limits and additional sampling of public water utilities serving <10,000 individuals as part of the UCMR3 program would greatly assist in further identifying sources of PFAS contamination for U.S. drinking water supplies.

Introduction

Poly- and perfluoroalkyl substances (PFASs) are a large group of persistent anthropogenic chemicals used in industrial processes and commercial products over the past 60 years.¹ Widespread use and extreme resistance to degradation have resulted in the ubiquitous presence of these compounds in the environment. The 2011-2012 U.S. National Health and Nutrition Examination Survey reported detectable serum concentrations of PFASs in virtually all individuals (97%).^{2, 3} Human exposure to PFASs has been linked to cancer, elevated cholesterol, obesity, immune suppression, and endocrine disruption.⁴⁻⁶ Health concerns in the early 2000s prompted manufacturers in Europe and North America to begin phasing out production of long-chain PFASs.⁷⁻¹⁰ These declines have been offset by increased production in developing regions such as Asia.⁸ Available data suggest widespread exposure to replacement (short-chain) PFASs also adversely affects human health.^{11, 12}

Human exposure to PFASs includes dietary sources, household dust, air, and drinking water.^{13, 14} High solubility of many PFASs means exposure from drinking water is a serious concern near contamination sources.^{15, 16} A number of regions across the U.S. have reported elevated PFAS concentrations in drinking water.¹⁵⁻¹⁸ Highest concentrations have been reported near industrial sites that produce or use PFASs.^{6, 16, 19} For example, perfluorooctanoic acid (PFOA) concentrations up to 13,300 ng/L were measured in drinking water near a fluorochemical facility in Washington, West Virginia where PFOA was used in fluoropolymer production.¹⁷ This level is 190-fold higher than the lifetime health advisory (70 ng/L) established by U.S. Environmental Protection Agency (US EPA)²⁰.

Many civilian airports and military fire training areas (MFTAs) have been contaminated by PFASs contained in aqueous film-forming foams (AFFFs) that are widely used during

69 firefighting training activities. Reported concentrations of PFASs in ground and surface waters
70 surrounding these sites are often three to four orders of magnitude higher than recommended
71 guidelines.^{21, 22} Wastewater treatment plants (WWTPs) are another important source of PFASs
72 because these compounds are not removed by standard treatment methods.²³ Biodegradation of
73 labile precursors increases concentrations of some PFASs in wastewater effluent relative to
74 influent.^{24, 25} Approximately half of the biosolids generated by WWTPs are disposed of through
75 land application and this practice may contribute to human exposure through subsequent
76 contamination of water, food, livestock, and wildlife.²⁶

77 Understanding nation-wide PFAS exposures from drinking water is important for
78 identifying potentially vulnerable populations. However, previous studies have mainly focused
79 on individual point sources of PFAS contamination and site-specific drinking water exposures.^{15,}
80 ¹⁶ Here we develop a statistical framework to investigate whether increased PFAS concentrations
81 in drinking water are associated with abundance of point sources within a watershed (represented
82 by an 8-digit hydrologic unit code, hereon abbreviated HUC). We used publicly available
83 drinking water concentrations of six PFASs from the US EPA's third Unregulated Contaminant
84 Monitoring Rule (UCMR3), including: perfluorobutane sulfonic acid (PFBS), perfluorohexane
85 sulfonic acid (PFHxS), perfluoroheptanoic acid (PFHpA), PFOA, perfluorooctane sulfonic acid
86 (PFOS), perfluorononanoic acid (PFNA) (Table S1).²⁷ We use this analysis to assess the utility
87 of the UCMR3 database for identifying sources that contribution to PFASs in drinking water,
88 vulnerable populations across the U.S., and priorities for future monitoring.

90 **Methods**

91 **Drinking water data**

Our analysis includes analytical results for six PFASs in 36,149 drinking water samples from the US EPA’s UCMR3 program collected between January 2, 2013 and December 9, 2015.²⁷ Samples cover all U.S. public water supplies (PWS) serving > 10,000 individuals (4,064 systems). Data are only available for 800 of the 144,165 PWSs serving <10,000 individuals. Minimum reporting levels (MRLs) for the six PFASs analyzed are listed in Table S1.

One limitation of the UCMR3 database is that specific locations of PWS system intakes are usually classified, making it difficult to place them within a specific hydrological network. We therefore extracted the zip codes for areas served by each PWS and aggregated data within 8-digit HUCs.²⁸ We selected the 8-digit HUCs to capture the most detailed hydrologic information that exceeds the spatial resolution of PFAS data (zip code areas). Our analysis was based on the highest reported concentration for each PFAS when multiple PWS systems are located within a single zip code and/or when multiple zip code areas are located within the same HUC. The UCMR program is designed to assess the prevalence of emerging contaminants in public drinking water supplies for potential regulation.

PFAS point sources

Our spatial analysis (Figure S1) included point source information for: (a) 16 industrial sites listed in the US EPA’s 2010/2015 PFOA Stewardship Program (Table S2);²⁹ (b) 8572 WWTPs;³⁰ (c) 664 military fire training sites located at 290 MFTAs;³¹ and (d) 533 civilian airports compliant with Title 14 Code of Federal Regulations, Part 139 for personnel trained in the use of AFFF (hereon referred “AFFF certified airports”).³² PFASs produced and/or used vary across industrial sites and not all compounds were associated with all sites. For example, a fluoropolymer and telomer manufacturer in Decatur, Alabama, produced both PFOS and

PFOA,³³ while a manufacturer in Parkersburg, West Virginia, only produced PFOA.³⁴ We conducted sensitivity analysis to examine the potential production misclassification bias by limiting industrial sites to include the ones that only produced or used each specific compound (Table S4). Comprehensive geospatial data for other potentially important PFAS sources, such as landfills and small industries that used PFASs, are not available and thus could not be included this analysis. We used the Google Maps API to geocode coordinates based on addresses.

Spatial and statistical analysis

We used ArcMap 10.3.1 (ESRI) to explore statistical associations between the abundance of point sources and PFAS concentrations within the same 8-digit HUC. We first tested for differences in abundance of point sources between HUCs with PFAS levels above and below detection. We then developed a multivariate spatial regression model that accounts and adjusts for correlations and co-location among point sources. The regression models focus on watersheds with detectable PFASs because high MRLs in the UCMR3 database limits the regions above detection. A natural log transformation was used to normalize the distribution of individual PFASs. PFNA and PFBS were excluded from the spatial regression analysis due to low detection frequency (15 and 14 out of 1601 watersheds, respectively). Positive spatial autocorrelation, driven by the tendency for nearby features to be more similar than distant features, is commonly seen in spatial data.³⁵ This will violate the assumption of independence in ordinary least squares (OLS) regression and yield biased estimates. Therefore, Moran's I statistic was used to test for spatial dependence in the model residuals from an OLS regression and correct for spatial dependence in the final spatial regression model. Akaike Information Criterion (AIC)³⁶ was used to compare the OLS and spatial regression models, where a lower AIC implies

a better model fit. A series of cross-validation tests were also completed to assess the predictive capacity and stability of the final set of models used in the analysis. The OLS and spatial regression models were constructed using GeoDa 1.6 software,³⁷ and cross-validation was implemented in R version 3.1.3.

Results and Discussion

PFASs in U.S. drinking water

PFASs were detected at or above the MRL in 194 out of 4,864 PWSs, serving 16.5 million residents located in 33 different states, three American territories (American Samoa, Northern Mariana Islands and Guam), and the Salt River Pima-Maricopa Indian Community. The majority (75%) of PWSs with detections were in 13 states: California, New Jersey, North Carolina, Alabama, Florida, Pennsylvania, Ohio, New York, Georgia, Minnesota, Arizona, Massachusetts and Illinois (Figure 1). Detection frequencies for PFASs above MRLs across the 4,864 PWSs were 2.2% for PFOA, 2.0% for PFOS, 1.7% for PFHpA and 1.1% for PFHxS and <0.003% for others.

Many detectable PFAS concentrations in the UCMR3 database are above chronic drinking water and water quality standards and may therefore pose appreciable health risks (i.e., surface water European Union: PFOS <1 ng/L; drinking water Sweden: sum of 7 PFASs < 90 ng/L; ground water State of New Jersey: PFNA <10 ng/L; drinking water State of Vermont: PFOA <20 ng/L for).⁴¹⁻⁴⁴ A recent analysis developed a benchmark-dose for immunotoxicity in children and suggested a drinking water limit of approximately 1 ng/L for PFOS and PFOA.²⁶ Data from rodents that measured sensitive endpoints such as mammary gland development support a similar level.²⁵

Six million people were served by 66 PWSs that have at least one sample at or above the US EPA's 2016 health advisory for PFOS and PFOA (70 ng/L combined). Concentrations ranged as high as 349 ng/L for PFOA (Warminster, Pennsylvania, zip code 18974), 1,800 ng/L for PFOS (Newark, Delaware, zip code 19702), and 56 ng/L for PFNA (Woodbury, New Jersey, zip code 08096).

The detection frequency in drinking water sourced from groundwater was more than twice that from surface water (Table S5). Long-chain PFASs (PFHxS, PFOS, PFOA, PFNA) were more frequently detected in groundwater and short-chain PFASs (PFHpA, PFBS) were detected more frequently in surface waters. This is consistent with the observation that PFAS mobility is inversely related to chain length.³⁸ PFASs are detectable in virtually all components of the environment.^{5, 7, 9, 13, 14, 19, 38, 39} Relatively high MRLs (10-90 ng/L) in the UCMR3 database are two orders of magnitude higher than the limit of quantitation in most published studies.⁴⁰ Thus, the large fraction of samples below reporting limits in UCMR3 (Table S5) is driven in part by high MRLs.

Sources surrounding locations with detectable PFASs

Drinking water samples from 1601 of the 2158 U.S. HUCs are included in the UCMR3 database. PFOA has the highest detection frequency (8%), and PFBS has the lowest (0.9%).

Point sources are significantly more abundant in HUCs with detectable PFASs (two-sided t-test, $p < 0.05$, Table 1, Figure S2). For example, HUCs with detectable PFOA levels have more industrial sites, MFTAs, AFFF certified airports, and WWTPs than those with concentrations below detection. These trends are observable across all PFASs. Similarly, HUCs with point sources have higher detection frequencies for PFASs (Table S3). For example, 10.4% of the

HUCs with no MFTA have a detection of any PFASs, but this percentage increases to 28.2% for HUCs with at least one MFTA.

Results of the spatial regression model

Spatial regression modeling explains 38-62% of the variance in drinking water concentrations of the four PFASs with high detection frequency (Table 2). Each additional industrial site within a HUC is associated with an 81% increase in PFOA ($p<0.001$, Table 2), which is the strongest statistical association across compounds and point sources. Increasing PFOS concentrations are positively associated with the number of industrial sites but this relationship is not statistically significant ($p=0.124$). The small number of sites that have manufactured or used PFOS may account for a lack of a statistically significant relationship.

Abundance of MFTAs within each HUC is positively associated with increasing levels of all four PFASs and is statistically significant for PFHxS and PFOS. Each additional MFTA within the same HUC is associated with a 20% increase in PFHxS ($p=0.002$), 10% increase in PFHpA ($p=0.155$), 10% increase in PFOA ($p=0.111$) and 35% increase in PFOS ($p<0.001$). AFFFs typically contain relatively high concentrations of PFOS and PFHxS and their polyfluorinated precursors compared to other perfluorinated carboxylates^{22, 45, 46}, which is consistent with these statistical results.

We find a small (1-2%) but significant increase in PFOS and PFOA with each additional WWTP within the same HUC. This is consistent with the greater abundance but smaller quantities of PFASs released by WWTPs.⁴⁷ The abundance of WWTPs is also an indicator of development and may be a proxy for other sources that discharge directly into the environment.

Similarly, results from Valsecchi et al.³⁹ show PFAS releases from WWTPs are important but less significant than fluorochemical manufacturing facilities in Italy.

Abundance of AFFF certified airports is not significantly associated with PFAS concentrations in the UCMR3 database. This may reflect misclassification biases resulting from using Part 139 certification to determine possible AFFF use at each airport. In addition, the UCMR3 database only has limited data for smaller PWSs where localized reports of contamination from airports have been most abundant.^{21, 48}

Current data limitations and future monitoring efforts

The UCMR3 database has several limitations that restrict its predictive power for identifying U.S. drinking water supplies likely to contain elevated levels of PFASs. Security concerns restrict disclosure of specific coordinates for PWS regions in most states and this limits the spatial resolution of UCMR3 dataset and associated statistical models to a radius of 50 km (median radius of watersheds).^{49, 50} Many of the impacted PWSs are groundwater systems and source zones for plumes of contaminated groundwater are often much smaller than 50 km.^{22, 46, 51}

Geospatial data are lacking for many potentially important point sources of PFASs that could be included in a spatial analysis such as a wide-range of industries, landfills, and municipal fire training areas.⁵²⁻⁵⁶ Data on PFAS releases from smaller industrial facilities (e.g., plastics, textiles, paper, lubricants) are usually withheld as confidential business information and little information on airborne emissions is available for characterizing the importance of atmospheric releases and potential long-range transport.

Sources not included in our spatial analysis are represented by the highly significant lambda (λ) coefficients (Table 2). Areas with high model residuals (greater than 1.5 standard

deviation) such as Colorado Springs, Colorado and Long Island, New York mean that current information on sources cannot fully explain the high observed PFAS concentrations. The map of model residuals (Figure S3) can thus be used to guide high priority sampling regions in future work.

We found statistically greater abundance of point sources in watersheds with detectable PFASs, including AFFF certified airports. However, multivariate spatial regression models did not show a significant association between AFFF certified airports and concentrations of PFASs in drinking water. Other studies have reported elevated PFAS concentrations in groundwater wells adjacent to AFFF certified airports.²¹ Small PWS regions and private wells may be disproportionately affected by PFASs originating from AFFF use at civilian airports but representative data for these drinking water sources are not included in the UCMR3 program.⁵⁷

Approximately 44.5 million U.S. individuals rely on private drinking water wells⁵⁸ that are not tested by the UCMR3 program. An additional 52 million individuals rely on smaller public water supplies (< 10,000 served) that also fall largely outside of (0.5% testing incidence) the UCMR3 program.⁵⁹ Monitoring data needed to evaluate PFAS exposures and risks from drinking water sources is therefore lacking for almost 1/3 of the U.S. population.

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Table 1. Mean abundance of point sources within 8-digit hydrologic unit codes (HUCs) with drinking water PFAS concentrations above and below method reporting limit in the UCMR3 program.

Compound	Mean abundance ^a within 8-digit hydrologic unit codes			
	Major industrial sites ^b	Military fire training areas	AFFF certified airports	WWTPs ^c
<i>PFBS</i>				
<90 ng/L (n=1587)	0.01	0.15	0.29	4.9
>90 ng/L (n=14)	0.21	0.71	0.50	14.6
<i>p-value</i> ^d	0.206	0.105	0.148	0.069
<i>PFHxS</i>				
<30 ng/L (n=1507)	0.01	0.13	0.27	4.8
>30 ng/L (n=94)	0.06	0.60	0.63	8.8
<i>p-value</i>	0.056	<0.001	<0.001	<0.001
<i>PFHpA</i>				
<10 ng/L (n=1509)	0.01	0.13	0.26	4.7
>10 ng/L (n=92)	0.09	0.57	0.67	9.7
<i>p-value</i>	0.016	<0.001	<0.001	<0.001
<i>PFOA</i>				
<20 ng/L (n=1473)	0.01	0.13	0.26	4.6
>20 ng/L (n=128)	0.05	0.52	0.56	9.5
<i>p-value</i>	0.038	<0.001	<0.001	<0.001
<i>PFOS</i>				
<40 ng/L (n=1487)	0.01	0.13	0.26	4.7
>40 ng/L (n=114)	0.05	0.54	0.57	8.9
<i>p-value</i>	0.064	<0.001	<0.001	<0.001
<i>PFNA</i>				
<20 ng/L (n=1586)	0.01	0.15	0.28	4.9
>20 ng/L (n=15)	0.13	1.13	1.13	20.1
<i>p-value</i>	0.366	0.014	0.008	0.007

^a Mean abundance is calculated as the mean numbers of point sources within HUCs with PFASs above or below-detection.

^b Only the major industrial sites participating in US EPA 2010/2015 PFOA Stewardship Program were included.

^c Wastewater treatment plant.

^d Two-sample t-test *p-values* are reported.

Table 2. Spatial regression models for drinking water PFAS concentrations as a function of abundance of point sources.

Compound	Major industrial sites ^a	MFTAs ^b	AFFF certified airports	WWTPs ^c	λ^d	R^2
<i>PFHxS</i>						
Coefficient ^e	24%	20%	-13%	1%	94%	0.62
<i>p-value</i> ^f	0.249	0.002	0.073	0.045	<0.001	
<i>PFHpA</i>						
Coefficient	10%	10%	-2%	0.5%	72%	0.40
<i>p-value</i>	0.569	0.155	0.761	0.436	<0.001	
<i>PFOA</i>						
Coefficient	81%	10%	-6%	2%	52%	0.38
<i>p-value</i>	<0.001	0.111	0.353	0.006	<0.001	
<i>PFOS</i>						
Coefficient	46%	35%	-6%	2%	79%	0.46
<i>p-value</i>	0.124	<0.001	0.512	0.007	<0.001	

^a Only the major industrial sites participating in US EPA 2010/2015 PFOA Stewardship Program were included.

^b Military fire training area.

^c Wastewater treatment plant.

^d Coefficient for the spatial error term characterizing spatial influence.

^e Results have been transformed to reflect expected changes in drinking water concentrations per increase in the abundance of different sources. Positive coefficients in the results indicate increasing concentrations with increasing abundance of point sources within the same hydrologic unit.

^f *p*-values for spatial error regression model. The spatial error term is used to incorporate spatial autocorrelation structures into a linear regression model.

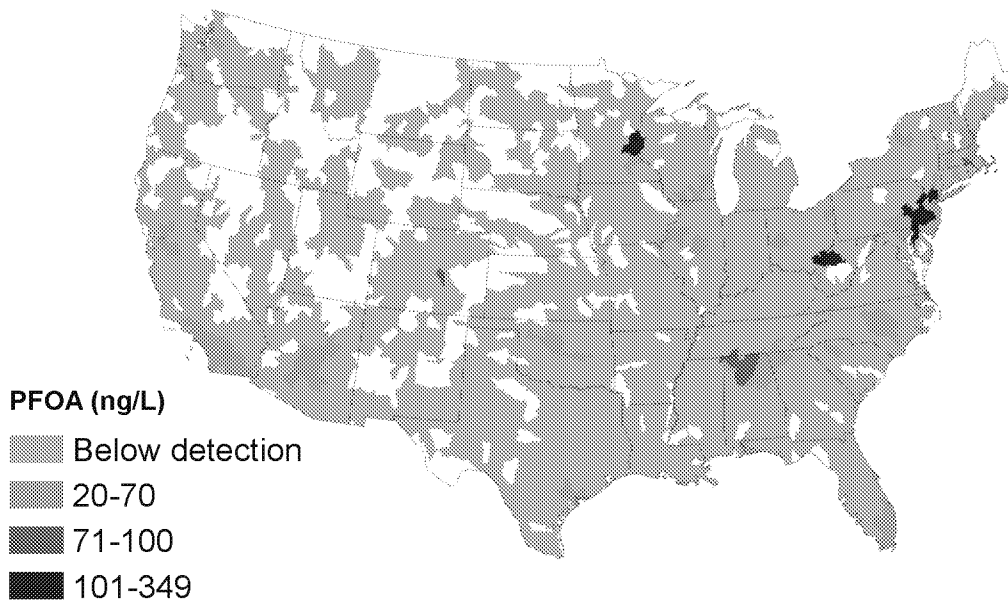
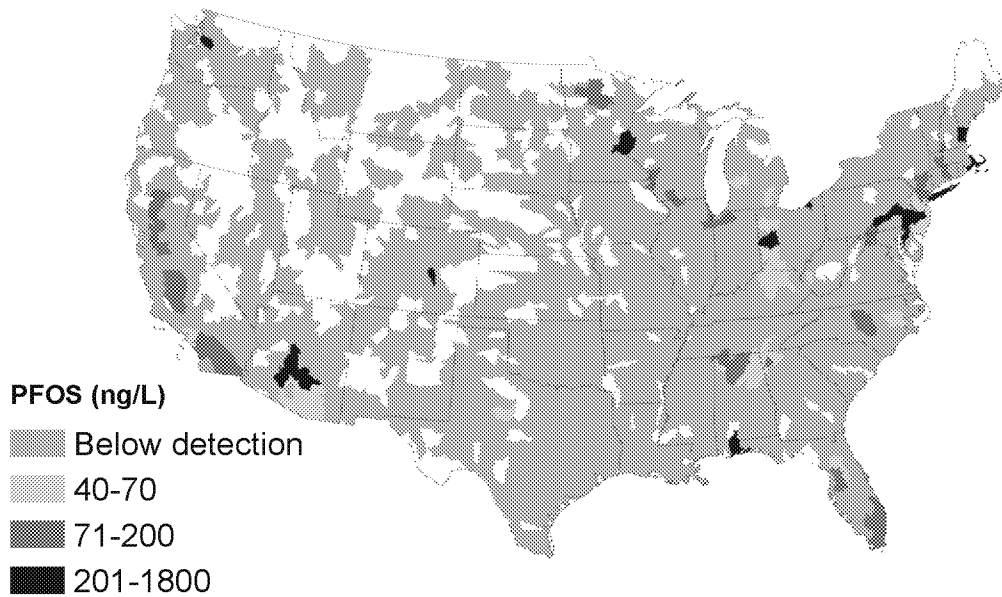
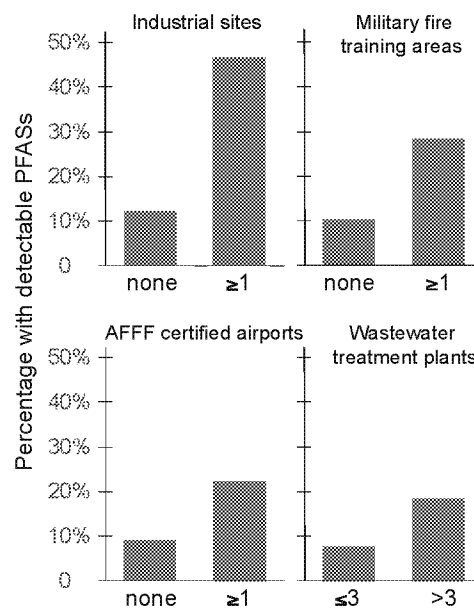
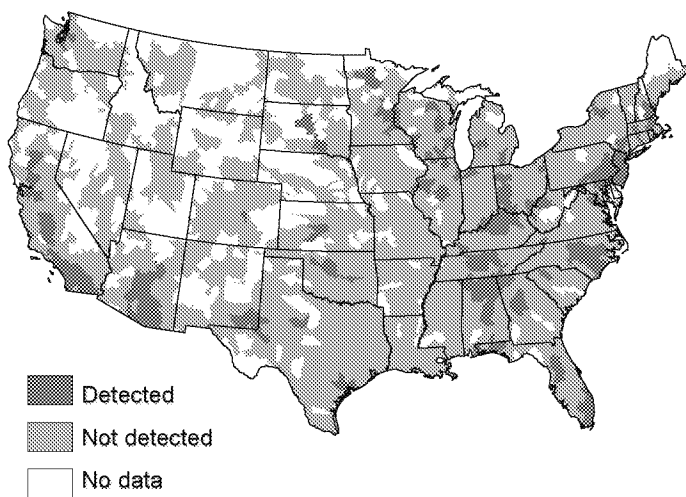


Figure 1. Hydrologic unit codes (8-digit HUCs) used as a proxy for watersheds with detectable PFOA and PFOS in drinking water measured in the US EPA's UCMR3 program (2013-2015). Blank areas represent regions where no data are available.

Hydrological units with detectable PFASs



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